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LASER-CHEMICAL ACTIVATION OF ALUMINA CERAMICS SURFACE

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The study of the process of laser-chemical activation of ceramic surface and its subsequent chemical metallization is described. The obtained results serve as the basis for the development of an industrial method for local metallization of the surface of products made of alumina ceramics.

Laser treatment of products of alumina ceramics VK-100 and VK-94-1 substantially modifies the structure and physicochemical properties of their surface [1, 2]. The most effective treatment is carried out by pulse or continuous IR-range lasers based on yttrium-aluminum garnet or carbon dioxide using a scanning beam of power density 10^4 – 10^5 W/cm^2 over the surface with a speed of 1 – 10 cm/sec. In this case significant modifications of structure and chemical composition occur within a ceramic layer 50 – 100 μm thick fused by laser radiation. Most of these modifications are related to the partial loss of oxygen and the transition of the crystalline structure of alumina from α-Al_2O_3 to γ-Al_2O_3, which is registered by x-ray phase analysis and IR spectroscopy methods. Another probable hypothesis assumes the formation of the AlO? radical-ion in the laser-treated ceramic layer, which is corroborated by electron paramagnetic resonance spectroscopy: an intense wide line with the *g*-factor more than 2.1 is formed, which at the nitrogen temperatures reveals a superfine structure of 12 lines [3, 4].

X-ray photoelectron spectra of the surface register as well a chemical shift of the line Al 2*p*, which presumably indicates a partial reduction of Al^{3+} in Al_2O_3 to Al^{2+} (Fig. 1). Furthermore, it is established that a laser-treated ceramic surface becomes saturated with carbon from atmospheric air. This increases by two orders of magnitude the concentration of carbon and changes the color of ceramics to dark gray (ceramics VK-100) or black (ceramic VK-94-1). The IR spectra in the range of 1100 – 1250 cm^{-1} exhibit a wide band caused by the stretching vibrations of the group >C=O. The band intensity and the degree of blackness significantly grow in the case of laser treatment of a ceramic surface covered by an organosilicon liquid layer (Fig. 2).

A distinctive feature of ceramic surfaces treated by laser radiation is their increased chemical activity which, for instance, allows for performing chemical metallization without additional activation. It is known that for a metal ion to be chemosorbed on the surface, it requires 2 or 3 electrons (depending on the valence of the metal):

$$Au^{3+} + 3e^- \rightarrow Au^0,\ Cu^{2+} + 2e^- \rightarrow Cu^0, \text{ etc.}$$

The initial ceramic surface covered by hydroxyl group OH has no free electrons; therefore, chemical precipitation becomes possible only after a chemical activation of the surface, using, for instance, palladium chloride. However, precipitation of metal becomes possible after laser treatment of the surface. This is evidence for the formation of centers on which electrons needed for metal reduction can emerge. Such centers could be carbon clusters or clusters of radical-ion AlO^+.

The process of chemical metallization in this case is caused by the formation of short-circuit galvanic couples on ceramic surface [5]. The electrochemical scheme of such galvanic couple, when a ceramic sample in immersed into a chemical gold-plating solution based, for instance, on gold-hydrochloric acid $H[AuCl_4] \rightleftarrows H^+ + [AuCl_4]^-$, has the following form:

$$(-)Al^{2+}|[AuCl_4]^-|C(+).$$

The process of oxidizing the aluminum radical-ion AlO^+ to Al_2O_3 occurs on the active electrode (anode):

$$Al^{2+} \rightarrow Al^{3+} + e,$$

whereas the process of gold reduction takes place on the other electrode (carbon);

$$Au^{3+} + 3e \rightarrow Au\downarrow.$$

It can be seen from the electrochemical scheme of the galvanic couple that gold ions are reduced on carbon inclusions, whereas the radical-ion AlO^+ becomes oxidized and transformed into γ-Al_2O_3. In this process metallic gold inclu-

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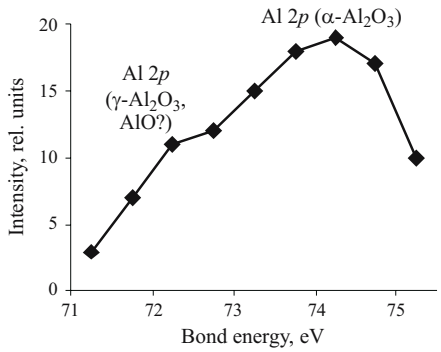

Fig. 1. Photoelectron spectrum Al 2*p* on the surface of Al_2O_3 treated by laser radiation.

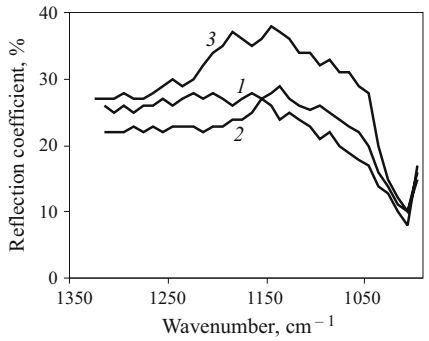

Fig. 2. IR reflection spectra of the surface of ceramics VK-94-1: *1*) untreated surface; *2*) surface laser-treated in air; *3*) laser-treated surface coated by organosilicon liquid.

sions are formed as clusters of size ranging from 0.1 to 2.0 μm. Gold clusters are nonuniformly distributed over the surface. Their quantity depends on the type of ceramics, the precipitation duration, and the power density of laser radiation. With a specific density of $10^4 – 10^5$ W/cm^2 and a precipitation duration of 10 sec their concentration is $10^5 – 10^6$ cm^{-2}. The maximum density of such clusters is registered on the structural defects of ceramics: microcracks, grain-pore interfaces, or along dislocation boundaries. It is established that the density of metal inclusions is the higher, the more numerous the ceramic defects and the higher the impurity content. Thus, ceramics VK-94-1 has a concentration of metal clusters an order of magnitude higher than ceramic VK-100 under equivalent laser and chemical treatment conditions.

As the exposure of the ceramic in electrolyte lengthens, the precipitation process becomes autocatalytic and the gold coating becomes continuous. Figure 3 gives the photo of metallized holes in VK-100 plates obtained in this way. Holes 150 μm in diameter and 500 μm deep were made in ceramics using a Kvant-12 pulse laser. The pulse duration was 2.5 msec and the pulse energy was 2 J. After perforating holes, ceramic substrates were subjected to chemical gold-plating for 5 min at a temperature of 60°C and the metal precipitated only on the surface of the holes. The coating thickness in the hole was around 1 μm and it is electric resistivity was not more than 0.1 Ω. Similar experiments were performed with chemical copper-plating solutions based on $CuSO_4$ with a HF additive. The rate of copper precipitation on laser-treated areas of ceramics reached 10 μm/min.

The performed studies have demonstrated the efficiency of laser-chemical activation of ceramic surface and have served as the basis for developing a method of local metallization of the surface of alumina ceramic products for the industry.

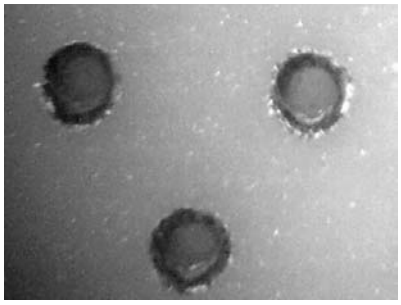

Fig. 3. Local metallization of inner surfaces of laser-perforated holes in ceramics VK-100.

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